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Method and Apparatus for forming a Film on a Substrate

This invention relates to a method and apparatus for forming a film on a substrate particularly, although not exclusively, to a film which is deposited on a semiconductor silicon wafer with flowing properties and retains carbon-containing groups on setting.

A number of methods have been disclosed for depositing a thin film on a semiconductor wafer, and examples included US 5314724, US 489753, US 5593741, EP-A-0731982 and EP-A-0726599. It can be seen from these that, up until recently, organic-containing silicon precursors have been processed or further processed in such a way as to avoid or subsequently remove organic components from the as-deposited film; this is, for example, disclosed in US 5314724. In addition, for some applications, it has been found to be difficult to retain both good film quality and good gap-fill capability on the surfaces and in recesses of a wafer on which the film is deposited.

According to a first aspect of the present invention, there is provided a method of forming a film on a substrate comprising:

(a)   positioning the substrate on a support in a chamber;

(b)   Supplying to the chamber in gaseous or vapour form a silicon-containing organic compound and an oxidising agent in the presence of a plasma to deposit a film on the substrate; and

(c)   setting the film such that carbon-containing groups

are retained therein.

The present invention provides a method of forming an unset film. Typically, the film is flowable (that is a film with a degree of surface mobility) and may thus provide good gap fill properties on the substrate.

It should be understood that without affecting the generality of this invention where gap fill properties are not required, e.g. for InterMetal Dielectric (IMD) layers on a semiconductor, then a flowing intermediate film will not be required. However the intermediate film deposited according to this invention will contain OH, which is almost entirely removed by the 'setting' process.

The formation of an OH and CH containing intermediate which is then further processed to remove OH but contain CH enables the formation of improved dielectric layers.

The substrate may be a semiconductor wafer, for example a silicon semiconductor wafer of the type known in the art.

Preferably, the oxidising agent is oxygen, although others could be used, for example H_2O_2.

For example, the silicon-containing organic compound may be an organosilane or an organosiloxane. Preferably, the silicon-containing organic compound is an alkylsilane, and even more preferably is a tetraalkysilane. In a particularly preferred embodiment of the invention, the silicon-containing organic compound is tetramethylsilane (TMS). However, for example, other organosilanes or

organosiloxanes could be used, one example being 1,1,3,3-
tetramethyldisiloxane (TMDS).

Experiments suggest that methoxysilanes, and in
particular methoxymethylsilanes, produce films with very
low dielectric constants and may be particularly preferred.

Particularly good results have been achieved with
cyclohexyldimethoxymethylsilane (CHDMMS) which has the
following structure:
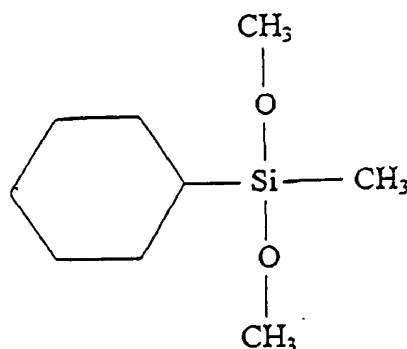
Experiments have also shown that a methoxysilane (e.g.
CHDMMS) may be able to be processed as in the above method
described, but without any oxidising agent present in the
plasma. It is supposed that this is because the Si-O bond
already exists as part of the methoxy group.

Accordingly, according to another aspect the invention
consists in a method of forming a film on a substrate
comprising:

(a) positioning the substrate on a support in a chamber;

(b) supplying to the chamber in gaseous or vapour form an
    organic compound including an Si-O bond to deposit a

film on the substrate; and

(c) setting (e.g. annealing) the film such that carbon-
containing groups are retained therein.

Preferably the compound is supplied in the presence of a

5   plasma, but other energy sources may be utilised to cause
appropriate deposition and these may be combined with spin-
on techniques.

The film may be deposited on a substrate positioned on
a low-temperature support for example, a support at a

10   temperature of about 0°C. Indeed temperatures in the range
0°C to 70°C have produced practical results, with
temperatures of 30° and 50°C proving particularly
practical.

In one embodiment, the method may further comprise

15   supplying RF power during deposition of the film. This RF
power is preferably applied to a showerhead or the like
through which the gaseous precursors are passed into the
chamber.

Whilst any suitable experimental conditions may be

20   used, it has been found that typical conditions include a
flow rate of 210 sccm tetramethylsilane, a flow rate of 200
sccm O_2, a chamber pressure of 2000 mT, a support
temperature of 0° and a showerhead temperature of 100°C,
and 250 watts of 380 khz RF power applied to the

25   showerhead, although it is pointed out that these are only
typical conditions.

The setting of the film may be carried out by an

annealing step, for example at a temperature of about 450°C which serves to remove water from the deposited film. It has been found that typical k value of the set film is about 2.55, for example for a 6000Å thick film deposited with a base layer (prior to deposition of the film) or capping layer (on the formed layer) after an annealing step at about 450°C in the absence of oxygen. This k value is a measure of the dielectric constant and it can be seen that the present invention provides a particularly low dielectric constant.

Alternatively, and often preferably, the setting step is performed by exposing the deposited film to an H_2 containing plasma without any prior heating of the film. In this connection it is preferred that the support is not biased during the deposition stage to avoid heating arising from ion bombardment.

According to a third aspect of the present invention, there is provided a method of forming a film on a substrate comprising:

(a) positioning the substrate on a support in a chamber;

(b) supplying to the chamber in gaseous or vapour form tetramethylsilane and oxygen in the presence of a plasma and a supply of RF power to deposit a film on the substrate; and

(c) setting the film such that carbon-containing groups are retained therein.

The setting step can be performed as set out above.

Particularly good results have been achieved with the H$_2$ plasma treatment without prior heating.

According to a further aspect of the present invention, there is provided an apparatus for forming a

5   film on a substrate, the apparatus comprising:

(a)   a support for the substrate positioned in a chamber;

(b)   means for supplying to the chamber in gaseous or vapour form a silicon-containing organic compound and an oxidising agent in the presence of a plasma to

10   deposit a film on the substrate; and

(c)   means for setting the film such that carbon-containing groups are retained therein.

The apparatus may, in one embodiment, further comprise means for improving the uniformity of the deposition of the

15   film on the substrate. This may be arranged in the region of, or around, a showerhead and, whilst the applicant is not to be restricted hereby, it is thought that its role in the uniformity of deposition is possibly as a result of providing a site for surface reactions about the surface

20   periphery thus enhancing deposition rate at the edge of the substrate.

Although the invention has been defined above, it is to be understood that it includes any inventive combination of the features set out above or in the following

25   description.

The invention may be performed in various ways and a specific embodiment will now be described, by way of

example, with reference to the accompanying drawings, an in which:

Figure 1 is a schematic view of an apparatus for use in the present invention;

Figure 2 is a Fourier Transform Infra-Red (FTIR) spectrum showing an as-deposited and annealed film according to this invention;

Figures 3(a) and 3(b) are scanning electron micrographs showing the annealed film formed by the present invention;

Figure 4 is a Fourier Transform Infra-Red (FTIR) spectrum for a first process run without oxygen;

Figure 5 is the equivalent FTIR for the process run with oxygen;

Figure 6 is a table showing initial experimental results using standard delivery systems for CHDMMS;

Figure 7 is a table showing experimental results using a syringe pump to deliver CHDMMS;

Figures 8 to 10 are FTIR spectrum relating to certain experiments identified in Figure 7;

Figure 11 shows FTIR plots for film formed from TMS after an anneal (FTM) process and after H_2 plasma processing when no anneal step has occurred;

Figure 12 is a graph of plots showing the affect of an FTM process, a 5 min H_2 plasma and a 10 min H_2 plasma on the thickness and the refractive index of a TMS based film;

Figures 13 to 15 are respective bar graphs indicating

the affects of an oxidising strip on FTM, 5 min H_2 plasma and 10 min H_2 plasma treated TMS + O_2 deposited films;

Figure 16 illustrates the film stress values pre- and post-oxidising strip, after various post film formation

5   treatment regimes;

Figure 17 sets out the dielectric constant of TMS films after various post formation regimes;

Figure 18 is a bar graph comparing the dielectric constant of layers treated by FTM, 5 min, 10 min and 30 min

10   H_2 plasma for a pair of substrates; and

Figure 19 is a SIMS plot for a TMS + O_2 deposited film which has been set with a 5 min H_2 plasma.

Referring to Figure 1, there is shown an apparatus generally at 1 which includes a vacuum chamber 2 having a

15   showerhead 3 and a wafer support or platen 4.   The showerhead 3 is connected to an RF source (not shown) to form one electrode, whilst the support 4 if preferably earthed.   Alternatively or additionally, the RF source could be connected to the support 4.   The showerhead 3 is

20   connected via pipes (not shown) to respective sources of tetramethylsilane and oxygen.   The apparatus is generally of the form disclosed in EP-A-0731982, which is incorporated herein by reference.   However, a standard (non-duplex) showerhead is normally used. Also shown is an

25   optional uniformity ring 5 arranged around the showerhead 3.   This ring 5 plays an active role in the uniformity of deposition of the film on the wafer and may be desirable

for some processes.

In use, the apparatus 1 is arranged to deposit a water and/or OH containing intermediate layer on a wafer which may be flowable and may be used to produce a planar layer or for "gap filling" for applications such as pre-metal dielectric, shallow trench isolation and intermetal dielectric on semiconductor devices. The film is formed by introducing into the chamber tetramethylsilane and oxygen in gaseous or vapour form and reacting them within the chamber. This forms an intermediate layer with a degree of surface mobility even when a plasma is present. It has been found that very small dimensioned gaps can be filled by the process of the present invention. This is not to restrict the invention as often process conditions may yield an intermediate layer containing OH that does not flow but still retains the other characteristics of this invention. The reaction takes place in the presence of a plasma. Subsequently, the film is annealed by heating, preferably in the absence of oxygen and most preferably in the presence of a hydrogen containing plasma.

Example

The precursor tetramethylsilane (TMS) has been applied with various other precursors, a platen temperature of approximately 0°C and RF power of either low (e.g. 380 Khz) or high (e.g. 13.56 Mhz) frequency where indicated. The basic results were as follows:

TMS + H_2O_2	No deposition in the pressure range up to 5,000 mT
TMS + $MeSiH_3$ + H_2O_2	Slight increase in carbon content over just $MeSiH_3$ + H_2O_2. Deposition rate ~ 6000 Å/min
TMS + DiH_4 + H_2O_2	No carbon in the film. Deposition rate ~ 900 Å/min
TMS + H_2O_2 + RF	Deposition rate ~ 400 Å/min. High refractive index
TMS + O_2 + RF	Deposition rate over 2 micron/min – high carbon content.

A 'preferred' process was then developed consisting of:

210sccm TMS (calculated from fill rate checks)

200sccm O_2

2,000 mT pressure

0° platen temperature and 100°C showerhead temperature

250 watts of 380khz RF power applied to the showerhead.

This yielded a k value of 2.55 (measured by CV techniques) for a 6,000 Å thick film deposited without base or capping after an anneal at approximately 450°C in the absence of oxygen.

Figure 2 shows a FTIR spectrum for an as-deposited and annealed film according to this aspect of the invention. The two spectra are shown overlain on the same diagram for ease of comparison. The as-deposited spectrum is the lower of the two and shows at 6 the characteristic peak of O-H bonds associated with water. Between 3,000 and 2,600 wave

numbers O-H bonds associated with free water, isolated O-H
and H bonded O-H are present. Water contains free water
and H bonded O-H and thus gives a characteristically broad
peak in this area. At 7 is the $C-H_3$ peak; at 8 is the Si-

5   CH_3 peak (Si-C); and at 9 is the Si-O peak.

It can thus be seen that a film has been deposited
containing water and/or OH which is subsequently removed by
the annealing step and that CH_3 is present, is bonded to Si
and remains in the film after annealing to form the hard

10   film.

Generally, an indicator of low k characteristics is a
high Peak Area Ratio(PAR) between Si-C and Si-O on the
FTIR. It is believed Si-C bonds block Si-O bonds and thus
reduce the density of the resultant film. Hence, a high

15   Peak Area Ratio Si-C:Si-O is indicative of a low k film.
It was however noted that for these plasma deposited and
annealed films the measured k values were not as low as the
Peak Area Ratio Si-C:SiO would suggest from non-plasma
deposited low k films. deposited from a reaction of

20   methylsilane and peroxide.

Films of this invention as annealed as shown in Figure
3 which demonstrate the flowing characteristics of the as-
deposited film.

In general, the following effect of changing the

25   parameters in a process have been observed:

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Parameter	Property			
	Refractive Index	FTIR Peak SiC/SiO	Area Ratio CH/SiO	Uniformity
Pressure increase	down	up	up	better
Power increase	none	down	up	better
Nitrogen flow increase	up	down	down	worse
TMs/O_2 ratio increase	down	up	up	none
Total TMS/O_2 decrease	none	down	down	none

An experiment has particularly been carried out using cyclohexyldimethoxymethylsilane (CHDMMS). As is reported below this has shown significantly reduced dielectric constants. It is anticipated that benefits will be found from many methoxysilane compounds such as tetramethoxysilane.

The experiments were carried out in a chamber substantially as shown in Figure 1, or in our co-pending British Patent Application 9914879.3, with an electrode gap spacings of 40mm and 20mm and the uniformity ring shield used for non-plasma based processes removed. The CHDMMS was fed into the chamber using a syringe delivery system described in our co-pending British Patent Application No. 9922691.2, which is incorporated hereinby reference, as opposed to a traditional low vapour pressure mass flow controller. This was done due to the fact that, as described below, CHDMMS could not be reliably delivered by conventional means as it has a relatively high boiling point (approximately 200°C) compared to most of the other precursor materials investigated in Application 9914879.3.

All processes were run with plasmas applied to the

showerhead.   All wafers were 'set' by annealing for

typically 30 minutes at approximately 480°C.

The following parameter ranges have been investigated:

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Pressure   —   500 mT to 1500 mT
Power (380 kHz)   —   50 W to 750 W
Platen temperature —   0°C to 70°C
CHDMMS flows   —   0.5 g/min to 1.5 g/min
Oxygen flows   —   0 to 200 sccm
10 Nitrogen flows   —   0 to 400 sccm
Peroxide flows   —   0 to 0.75 g/min

It will be appreciated that the relative flow rates

are particularly relevant to the process.   In general

15 higher rates lead to higher deposition rates and thus a

broad range of flow rates can achieve similar results.

Thus values outside the above ranges may be applicable.

Two particularly preferred process examples are given

below: one of these is with oxygen and one is without

20 oxygen.

Process 1 (no O₂)	
Pressure	900 mT
Power	500 W
Platen temperature	50°C
CHDMMS flow	0.85 g/min
Nitrogen flow	200 sccm

Process 2 (with O₂)	
Pressure	900 mT
Power	250 W
Platen temperature	50°C
CHDMMS flow	0.85 g/min
Oxygen flow	50 sccm
Nitrogen flow	150 sccm

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The resultant films were annealed and the post anneal results were as follows:

Process 1 (no O_2)	
Deposition rate	17000Å/min
Uniformity (max/min)	± 4%
Refractive index	1.370
Dielectric constant	2.55

Process 2 (with O_2)	
Deposition rate	9500Å/min
Uniformity (max/min)	± 5%
Refractive index	1.340
Dielectric constant	2.25

5   As can be seen the dielectric constants in each case are desirably low, but the "with oxygen" process is significantly advantageous.

Figures 4 and 5 show the respective FTIR spectra post anneal. It will be seen that they are substantially

10   similar. The feature between 2500 and 2000 in Figure 5 is believed to result from atmospheric (background) CO_2.

In fact, initial experiments were carried out using a CHDMMS source consisting of a PTFE pot within an evacuated aluminium vessel which was heated to 150°C. The pot was

15   connected by gas line to a gas mass flow controller suitable for H_2O with a conversion factor of 1.000. The RF power was applied to the showerhead with a spacing from the wafer of 40mm. The RF was 380khz continuous mode. Results from these experiments are shown in Figure 6. The numbers

in the CHDMMS column are the nominal gas flow as measured by the mass flow controller however stable flows could not be achieved and therefore these results are for near random quantities of CHDMMS being delivered to the process

5   chamber. At this point experimentation was halted until a superior delivery system for this precursor could be developed.

CHDMMS has a boiling point of 201.2°C, and a density of 0.940 g/cc. As it was noted in these experiments that

10   CHDMMS deposits a low k insulator without the addition of an oxidising agent it is therefore possible that it could be delivered as a liquid to a semiconductor wafer without a chamber being required (e.g. by well known 'spin-on' techniques) and then reacted either thermally or by plasma

15   to form a low k (k<3) insulator layer. The apparatus used may in effect deposit a liquid by vaporising the liquid precursor, delivering it as a vapour and then condensing it onto the wafer at a temperature below the boiling point of the precursor at that pressure. It is not yet clear if the

20   reactions to the precursor take place on the wafer or at some other place, depositing reaction products onto the wafer.

Having developed a more suitable liquid delivery system which utilises a syringe pump, further experiments

were carried out as shown in Figure 7. From these experiments preferred processes were developed as further described here. FTIR for runs 13, 14 and 16-23 of Figure 6 respectively are illustrated in Figures 8 to 10.

5   Further experiments have been carried out using the following conditions:

Pressure:	2500 millitorr
RF Power at 13.56 Mhz	250 watts/200mm wafer
Showerhead temperature	100°C
TMS flow	100sccm (approximately)
Oxygen flow	100sccm
Nitrogen flow	500-600sccm

The ratio of TMS (tetramethylsilane) to oxygen is the same as previously (approximately equal quantities), but at half the total flow rates. In this preferred process nitrogen has been used, primarily as a dilutant.

Thermal treatment step ("setting" or "anneal")
Time	5 minutes
Pressure	10 torr nitrogen (no oxygen)
Wafer temperature	400°C approximately

In the process above, where the process platen temperature was varied, the results were as follows

T °C	Rate Å/min	Non-Uniformity % max/min	FTIR SiC/SiO	SiH/SiO	CH/SiO	RI av.	Dielectric constant
10	7,778	2.7	0.0608	0.0060	0.0287	1.3825	2.72
20	7,673	3.8	0.0594	0.0057	0.0280	1.3832	2.72
30	7,589	4.8	0.0588	0.0059	0.0282	1.3791	2.65
45	7,543	3.1	0.0584	0.0056	0.0273	1.3867	2.70
55	not recorded		0.0527	0.0044	0.0234	not recorded	2.75
60	6,968	3.9	0.0512	0.0074	0.0293	1.3935	2.69

Once more the initial deposition process puts down a water and/or OH containing intermediate film which needs to be set to substantially remove the water and/or OH to create a low k layer. For the purposes of the above

experiment this setting was achieved by a thermal treatment step as indicated. However other post deposition processes have been experimented with, as can be seen below. The significant features of this experiment were both the

5   continued achievement of a dielectric constant below 3 and the observation that both the refractive index (which is believed to be a measurement of density) and the dielectric constant dipped when a platen temperature of 30° was used. These results are consistent with the normal understanding

10   that dielectric constant and density are related for a specific film composition, so that lower refractive index will normally indicate a lower dielectric constant.

Subsequent to this experiment a further set of films were formed using the following process matrix:

15   • TMS   –   100 sccm

     • O2   –   100 sccm

     • N2   –   600 sccm

     • Pressure   –   2000 mT

     • Substrate support–   30°C, DC ground potential

20   (unbiased)

     • Power   –   250 Watts High Frequency 13.56 MHz

                                to the showerhead

The films resulting from this process were set either by the annealing process (which is hereinafter referred to

as FTM treatment) or process and/or by treating the film

with an H_2 plasma treatment.

The FTM process was as follows:

- Wafer temperature   450°C

- Pressure   10 Torr (Nitrogen)

- Time   3-5 minutes

The H_2 plasma treatment was as follows:

- Hydrogen   -   1000 sccm

- Pressure   -   4000 MT

- Temperature   -   400°C

- Power   -   2000 Watts High Frequency 13.56 MHz

                       to an electrode opposed the wafer

- Time   -   Depends on thickness but typically 3

                       minutes for 6kÅ although longer times

                       appear to lead to lower K.

Alternatively other RF frequencies could be used applied to

any electrode or electrodes either internal or external to

the wafer containing chamber such as to create or sustain

ionised hydrogen species adjacent to the film to be

treated.   This   is   to   include   remote   plasma   sources

including microwave and inductively completed RF sources

wherever situated.

The H_2 plasma may also contain other components e.g.

effectively inert dilutants for example argon, helium or

other gasses or vapours that do not detract from this treatment.

Figure 11 shows respective FTIR plots for the film prepared as described above and then treated by FTM or by plasma. Beneath each chart is an indication of the bonding ratios between various components. As will be understood by a man skilled in the art the slope of the graph is not relevant in a FTIR plot; it is only the peaks which provide information. The relative heights of the peaks are indicated by the ratio tables and it will be seen that there is a significant reduction in the bonding between the various components in a plasma treated film as compared with one that has had the FTM post deposition treatment. This indicates that the hydrogen plasma treated intermediate film is structurally different from the FTM treated intermediate film.

In Figure 12 the upper plot indicates that there is no significant difference in film thickness between the various post treatment processes, but there is a significant driving up of the refractive index the longer a plasma treatment takes place. Indeed after a 10 minute H_2 plasma, the refractive index is approaching that of pure SiO. Normally, as has been explained above, this would be expected to result in a significant increase in dielectric

constant, but as can be seen in Figure 17 an increase in the period of the H_2 plasma treatment simultaneously produces a significant decrease in the dielectric constant, provided that the film is not subject to heat treatment

5   prior to the plasma treatment. Thus after a 10 minute H_2 plasma treatment the OH containing film is set and has a dielectric constant of below 2.2, which is an extremely low figure typically unachievable by chemical vapour deposition means.

10   It will be noted that a very short H_2 plasma treatment (e.g. 1 minute) does not render the film totally stable nor does it reduce significantly the dielectric constant below an FTM anneal although the film is still comparable with other reported films. Wet etch rate experiments have

15   demonstrated that the hydrogen plasma treatment starts at the top of the film. The longer the plasma process, the greater the depth treated the lower the k value of the treated film. The hydrogen plasma treated film etches considerably (e.g. 20 or more times) slower than the FTM

20   treated film. It will also be observed that an H_2 plasma treatment is also not effective in reducing dielectric constant after a previous heating or anneal step.

Turning now to Figures 13, 14 and 15 it will be seen in Figure 13 that film which has had the FMT treatment

appears to be very susceptible to an oxidising process e.g. a photoresist strip with carbon and hydrogen seemingly being removed from the material.   This is not totally surprising, because such an oxidising process was

5   previously used to remove such materials in the film (in particular organics from precursors) before it was appreciated that they might have a beneficial affect on the dielectric constant.   Figures 14 and 15, on the other hand, show that the plasma treated films are substantially

10   unaffected by the oxidising photoresist strip process. This is of course important, because it makes it much easier to remove resist from the surface of the dielectric layer without damaging that layer.   Figure 16 shows that the plasma treated films also have particularly low stress

15   values whether before or after the oxidising strip.

It is believed that similar results would be achieved with most flowable or water and/or OH containing films that retain carbon, more particularly CH, in the finally used dielectric layers.

20   Thus the inventors have, in particular determined a process for depositing a flowable or at least OH containing intermediate film which is subsequently set using heat in the absence of oxygen and preferably in the presence of an H_2 containing plasma with the result that the film has a

dielectric constant below 3 and, with the application of hydrogen plasma, a reduced dielectric constant and a good resistance to oxidising strip.   It is postulated that this combination results from the surprising fact that H_2 treatment reduces the dielectric constant whilst increasing the refractive index and hence, almost certainly the density as evidenced by a greatly reduced wet etch rate.

Further evidence for this is illustrated in Figures 18 and 19.   Figure 18 shows that progressive treatment by H_2 plasma drives down the dielectric constant, with samples treated for 30 minutes achieving a k of 1.8.

Figure 19 provides analysis of the hydrogen plasma treated film has been carried out as follows:

SIMS (secondary ion mass spectrometry) data of a TMS + O_2 deposited film that has been hydrogen plasma treated for 5 minutes has been generated.   [The horizontal axis is through the depth of the sample starting at just above the surface and ending in the silicon wafer. What is shown is an organic contaminated (high C) sample surface (to be ignored), followed by a 'true' analysis].

The SIMS profile shows a film surface depleted of carbon and hydrogen by the hydrogen plasma treatment.   This is a not unsurprising result and is consistent with a measurable difference in the dielectric constant of this

surface layer and the bulk of the film. When this surface is etched away the remainder of the film (adjusted for it's reduced thickness) has a lower dielectric constant than the whole of the film including this surface layer. Yet the whole film including this carbon depleted surface has a lower k value than an FTM treated film.

Wet etch rate experiments show that the hydrogen plasma treatment commences at the upper surface and progresses through the film. The hydrogen plasma treated film wet etches considerably more slowly than an FTM treated film and thus provides clear evidence that depth of treatment increases with plasma treatment times.

It is postulated that the hydrogen plasma treatment effectively replaces $Si-CH_3$ in the film with $Si-CH_2-Si$ (by intermediate reactions in which hydrogen ions and radicals play a part) with increased Si-Si linkage responsible for the increase in the refractive index.